

Chapter III

Results and Discussion

3.1) The preparation of styrene oxides from styrene.

The Alkali-Catalyzed Epoxidation reaction was used to synthesize styrene oxide. This new epoxidation and oxidation technique has been discovered in which dilute hydrogen peroxide (30-50%) was utilized under essentially neutral conditions. Thus, reaction of styrene with hydrogen peroxide in the presence of acetonitrile as co-reactant gave styrene oxide. The sequence of the reaction was shown in Eq. 1.13 (1) and Eq. 1.16. Styrene oxide was obtained in 66% yield and its identity was verified by the following spectral evidences.

3.1.1) The spectral data of styrene oxide.

The spectral data of styrene oxide were shown below :

IR ν (cm^{-1}) : 3100-3000, 2000-1800, 1700, 1120 (Fig 3.1)

PMR (CDCl_3) δ (ppm) : 2.80-2.84(1H), 3.14-3.19(1H),
3.87-3.90(1H), 7.30-7.38(5H) (Fig 3.2)

CMR (CDCl_3) δ (ppm) : 51.17, 52.36, 125.56, 128.21, 128.54, 137.69
(Fig 3.3)

MS m/e (percentage, int) : 120(M^+ , 42), 119(73), 91(96), 89(100)
63(22) (Fig 3.4)

The IR spectrum of styrene oxide (Fig 3.1) gave important absorption at 3100-3000 cm^{-1} of =C-H stretching of aromatic ring, 1600-1400 cm^{-1} of C=C ring stretching of aromatic ring, 1210 cm^{-1} of symmetric stretching of epoxide ring and 775, 920 cm^{-1} of asymmetric stretching of epoxide ring. IR spectrum

also indicated some impurity peaks such at 1710 cm^{-1} that would be a carbonyl group.

The **PMR** spectrum (Fig 3.2) showed the signal of styrene oxide at δ 2.80-2.84 ppm (1H), 3.14-3.19 ppm (1H) which was assigned as a quartet of CH_2 group of styrene oxide. The triplet at δ 3.87-3.90 ppm was the -CH- proton of styrene. The singlet δ 7.30-7.38 (5H) was aromatic protons.

The **CMR** spectrum (Fig 3.3) showed six signals that corresponded to eight carbon atoms in this compound. The chemical shift at 51.17 ppm was assigned to be carbon of CH_2 group and at 52.36 ppm was CH group. The chemical shift at 125.56, 128.21, 128.54, 137.69 ppm were carbons in aromatic ring.

The **MS** spectrum (Fig 3.4) displayed the molecular ion at m/e 120 (M^+ , $\text{C}_8\text{H}_8\text{O}^+$) and other fragmentation ion peak at m/e 119 (M^+-H , $\text{C}_8\text{H}_7\text{O}^+$), 91 ($\text{M}^+-\text{CH}_2\text{O}$).

To further study the constituent of the product mixture, gas Chromatography/ Mass spectrometry was used. The **GC/MS** spectrum data were shown in (Fig 3.5, 3.6, 3.7). The GC chromatogram showed four peaks at 7.99, 9.90, 11.53, 11.75 min., The NIST library search revealed that the retention time of 7.99 min. was styrene. The peak at 9.90 min.(mass spectrum in Fig 3.8) was benzaldehyde. It's an impurity in starting material. The peak at 11.53 min. was benzeneacetaldehyde (Fig 3.9). It's a by-product of reaction. The last peak at 11.75 min. was styrene oxide peak which its mass spectrum shown in Fig 3.4.

Table 3.1 The composition of reaction products.

Retention Time(min)	Components
7.99	styrene
9.90	Benzaldehyde
11.53	Benzeneacetaldehyde
11.75	Styrene Oxide

3.1.2) The optimum condition of epoxidation reaction.

In order to find the optimum condition of epoxidation reaction, temperature, concentration of styrene and concentration of hydrogen peroxide were varied. the ratio of styrene oxide to the styrene monomer was monitor by mean of GC/MS.

Table 3.2 showed the ratio of styrene oxide to styrene monomer. It indicated that at 50 °C the ratio SO/SM was the highest. At 10 °C and 25 °C the reaction might be too slow while at 70 °C some of the peroxide species might be decomposed.

Table 3.2 The ratio between styrene oxide and styrene monomer obtained at various temperature (°C) (Fig 3.10)

Temperature (°C)	Ratio of SO/SM
10	0.8626
25	1.0085
50	3.6157
70	1.4362

All other parameters were fixed as follow:

Styrene monomer	50 ml.(0.437 mole)
Methanol	186 ml.(4.597 mole)
Acetonitrile	64 ml.(1.246 mole)
Hydrogen peroxides	34 ml.(1.246 mole)

Table 3.3 showed the ratio of SO/SM when the amount of styrene was varied. It indicated that the optimum amount of styrene was 0.44 mole while the amount of methanol, acetonitrile and hydrogen peroxide were kept constant and the temperature was 50 °C.

Table 3.3 The ratio between styrene oxide and styrene monomer obtained from the reaction with various amount of styrene (Fig 3.11)

Styrene (mole)	Ratio of SO/SM
0.2185	2.279
0.4370	2.904
0.6555	0.3924
0.8740	0.2754

All other parameters were fixed as follow:

Methanol	186 ml. (4.597 mole)
Acetonitrile	64 ml. (1.219 mole)
Hydrogen peroxide	34 ml. (1.246 mole)
Temperature	50 °C

Table 3.4 showed the ratio of SO/SM when the amount of hydrogen peroxide was varied. It indicated that the optimum amount of hydrogen peroxide was 1.25 mole while keeping acetonitrile at 1.22 mole and styrene at 0.44 mole. If the concentration of hydrogen peroxides was too high used, it would react with *percarboximidic acid* (Eq 3.1 and 3.2) instead of reacting with acetonitrile. Therefore, percarboximidic acid was destroyed and up with less amount of product.



Table 3.4 The ratio between styrene oxide and styrene monomer obtained from reaction with various amount of hydrogen peroxide (Fig 3.12)

Hydrogen Peroxide (mole)	Ratio of SO/SM
0.5500	0.2290
0.8088	0.3297
1.2460	2.9040
1.2940	0.3338

All other parameters were fixed as follow:

Styrene 50 ml. (0.437 mole) Methanol 186 ml. (4.597 mole)

Acetonitrile 64 ml. (1.219 mole)

In this study, pH was not varied, because the product was only stable in neutral condition. From many results in the experiments, the best condition for synthesis of styrene oxide was 0.44 mole styrene, 4.597 mole methanol, 1.219 mole acetonitrile, 1.246 mole 50% hydrogen peroxide and pH 7-8 (about 7.5).

3.2) The preparation of 2-phenyl ethanol from styrene oxide.

The synthesis of 2-phenyl ethanol was carried out in the a pressure reactor using styrene oxide as starting material and Raney Ni as catalyst. the yield of 2-phenyl ethanol was 57%. The identity of the product was verified by spectral evidences. The only major impurity was ethylbenzene which could come from the reduction of unreacted styrene or could come from over reduction of styrene oxide itself. Nevertheless, ethylbenzene could be easily separated from 2-phenyl ethanol by distillation.

3.2.1) The spectral data of 2-phenyl ethanol are as follows:

IR ν (cm^{-1})	: 3600-3200, 2950-2875, 1600-1400, 1050, 750,710 (Fig 3.13)
PMR (CDCl_3) δ (ppm)	: 2.85-2.92(2H), 3.07(1H), 3.79-3.86(2H), 7.26-7.37(5H) (Fig 3.14)
CMR (CDCl_3) δ (ppm)	: 39.28, 63.46, 126.40, 128.56, 129.15, 138.95 (Fig 3.15)
MS m/e (percentage)	: 122 M^+ , 91, 77 (Fig 3.16)

The **IR**. spectrum of 2-phenyl ethanol (Fig 3.13) gave important absorption at 3600-3200 cm^{-1} of -OH stretching of alcohol, 3100-3000 cm^{-1} of =C-H stretching of aromatic ring, 1600-1400 cm^{-1} of C=C ring stretching of

aromatic ring, 2950-2875 cm^{-1} of $-\text{CH}_2$ group in 2-phenyl ethanol, 1050 cm^{-1} of CO:

The **PMR**. Spectrum (Fig 3.14) showed the signal of 2-phenyl ethanol at δ 2.80-2.84 ppm (2H, t, $J_A=6.843$ Hz), 3.79-3.86 ppm (2H, t, $J_B=6.841$ Hz) was doublet of CH_2 group, δ 3.07 ppm (1H) of proton in hydroxyl group. The chemical shift at δ 7.26-7.37 ppm (5H) was indicated protons in aromatic ring.

The **CMR**. Spectrum (Fig 3.15) showed the signal of 2-phenyl ethanol at 39.28 ppm (C-O) and 63.46 ppm was the carbon that connected to aromatic ring. The other's signal at 126.40, 128.57, 129.15 and 138.95 ppm was carbons in aromatic ring.

The **MS** Spectrum data (Fig 3.16) displayed the molecular ion at 122 amu. (M^+ , $\text{C}_8\text{H}_{10}\text{O}^+$) and 91 amu. ($\text{M}^+-\text{CH}_2\text{O}$).

3.2.2) The optimisation of hydrogenolysis reaction.

In order to find out the optimum condition for the hydrogenolysis of styrene oxide pressure of the reactor was varied. The reaction was monitored by GC/MS. According to table 3.5, the optimum pressure was 400 psi which was the maximum pressure attainable by the reactor. The reaction time was 6 hours.

Table 3.5 The ratio between ethylbenzene and 2-phenyl ethanol at various pressure of reactor Fig 3.17 and 3.18

Pressure (psi)	Ratio of P.A./E.B.
200	0.7768
300	0.7635
400	2.1123

Table 3.6 indicated the optimum amount of styrene oxide to be 0.13 mole to 0.1 g Raney Ni.

Table 3.6 The ratio between ethylbenzene and 2-phenyl ethanol obtained from reaction with various amounts of styrene oxide Fig 3.19 and 3.19

Styrene Oxide (ml)	Ratio of P.A./E.B.
0.0437	2.1123
0.0875	2.4177
0.1312	13.324
0.1750	5.6186

All other parameters were fixed as follows:

Pressure : 400 psi Ethanol : 1.279 mole
 Raney Ni : 0.1 g. Time : 3 hr.

Two experimental conditions were varied to find out the optimum condition. The first one was pressure of reactor, It's the most significant factor

affecting the quantity of product. In this research, high pressure at 400 psi was shown to give the highest ratio of 2-phenyl ethanol and ethylbenzene. The second factor was the concentration of styrene oxide. The hydrogenolysis of styrene oxide was complete, as indicated by GC/MS chromatograph which consisted of two peaks. It consisted of ethylbenzene at 7.25 min.. Mass spectrum of this compound was shown in Fig 3.21. The second peak at 12.97 min. was 2-phenyl ethanol (Fig 3.16). The best condition to convert styrene oxide to 2-phenyl ethanol was styrene oxide 0.13 mole, ethanol 1.28 mole, 0.1 g Raney Ni, at 400 psi.

3.3) The preparation of 2-phenyl ethanol from styrene waste.

] According to the manufacturer's information the styrene waste composed of various components shown below. The major component was styrene monomer. Therefore, styrene waste should be able to undergo epoxidation reaction with subsequent catalytic hydrogenation to give 2-phenyl ethanol.

Table 3.7 The composition of styrene waste.

Composition	amount
Styrene	98.86 %
Ethyl benzene	0.63 %
o-Xylene	166 ppm
m & p-Xylene	105 ppm
Cumene	478 ppm
p-methyl styrene	0.23 %
Other	588 ppm
Polymer Content	More than 1.26 %

after styrene waste was subjected to the optimized epoxidation condition reaction followed by catalytic hydrogenation described above, 2-phenyl ethanol was obtained in 57.39% yield. This result assured the rationalization that styrene waste could be able to convert to a more expensive product, 2-phenyl ethanol in reasonable yield. Therefore, synthetically and commercially aspect of this hypothesis is feasible. However, large scale synthesis should be carried out in order to learn more on the reaction condition. Due to the unavailable of large scale equipment, large scale synthesis can not be carried out during this study.



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